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SYNTHESIS AND SINTERING OF MONOLITHIC AND COMPOSITE CERAMICS UNDER HIGH PRESSURES AND HIGH TEMPERATURES

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Abstract: This paper summarizes the research and developmental activities, carried out at the High Pressure Laboratory, NAL, Bangalore, for the synthesis and sintering of ceramic materials (both monolithic and composites) under high pressures and high temperatures. A number of processing techniques namely, high pressure sintering (HPS), high pressure self-combustion synthesis (HPCS), high pressure reaction sintering (HPRS), reactive hot pressing (RHP), fabrication of ceramic-ceramic composites through intermediate soft phase processing (ISPP), reaction sintering of intermetallic matrix-ceramic composites were explored. These processing techniques were used effectively to fabricate sintered ceramic compacts with density ~ 99% of the theoretical density. In many of the cases, especially for the development of materials for the high temperature applications, no liquid phase forming additives were used. Extensive characterization of the sintered compacts was carried out to establish (i) the mechanisms of reaction and densification, (ii) microstructural evolution during synthesis, and (iii) microstructure-property relationship.

Key words: Ceramics, ceramic-ceramic composites, intermetallic matrix-composites, high-pressure sintering, high-pressure self-combustion synthesis, reactive hot pressing, SiC, TiB_2, TiB_2-TiC, NiAl, NiAl-TiB_2.

1. INTRODUCTION

Ceramics are a promising class of materials because of their high melting point, hardness and elastic modulus, and low thermal and electrical conductivity. Advanced ceramics have great impact on the market areas where high temperature is coupled with the demand for wear resistance and corrosion resistance. However, ceramic materials are not easy materials to work with, and the benefit of the unlimited availability of raw materials compared with metals is by far surpassed by the difficulties encountered during synthesis. Generally, ceramic powders are consolidated into dense solid bodies by reaction sintering, pressureless sintering, hot pressing with or without sintering aids. In most of the cases, consolidation by solid state sintering requires very high temperature (> 2400 K) and long sintering time (> 60 min). The exposure of the powders (high specific surface area) to high temperatures for a long time results in exaggerated grain growth during sintering. The sintered compacts thus produced have coarse grain size and inferior mechanical properties. The problem becomes uncontrollable when the starting powders are of sub-micron size, which is the requirement for producing advanced ceramics with superior mechanical properties. The sintering temperature and time can be lowered by addition of suitable sintering additives. But, in this case, a low melting second phase is inevitable at the grain boundaries which has adverse effects on the high temperature mechanical properties.

The present research program was undertaken to develop ceramics (both monolithic and composite) for wear resistance and high temperature applications. Where ever possible, the addition of sintering additives was avoided. A number of processing techniques was used to fabricate sintered compacts with near full density. These are (i) high pressure sintering (HPS), (ii) high-pressure self-combustion synthesis (HPCS), (iii) high-pressure reaction synthesis (HPRS) (iv) reactive hot pressing (RHP), and (v) fabrication of ceramic-ceramic composites at moderate pressures and temperatures through inter-

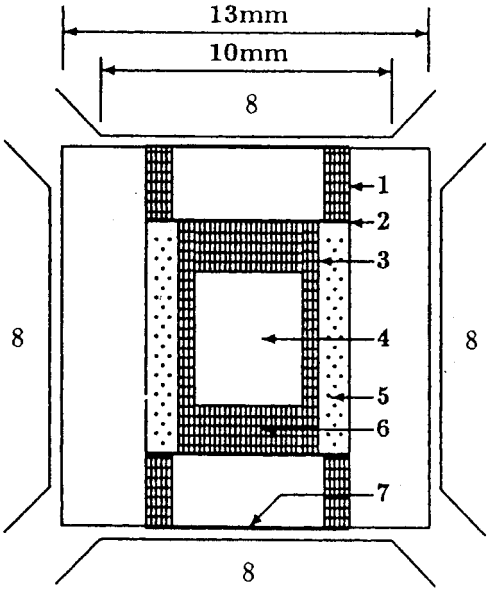


Fig.1. High pressure high temperature cell: (1) current ring (graphite), (2) graphite disc, (3) graphite heater, (4) sample, (5) zirconia liner, (6) graphite plug, (7) tantalum disc, (8) WC anvils; remaining portion of the cell is pyrophyllite.

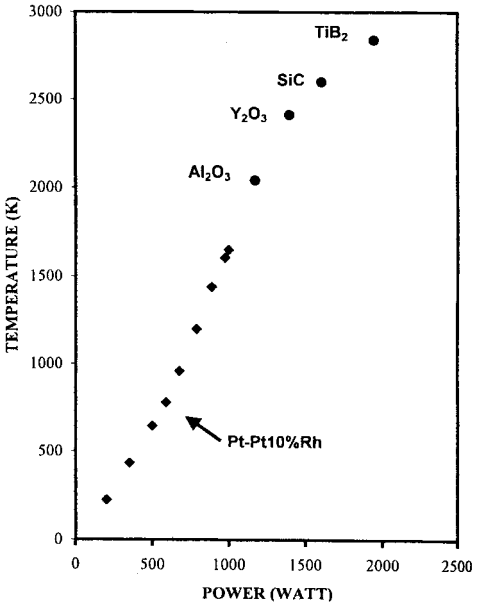


Fig.2. Power temperature calibration curve. Up to 1900 K, the curve was obtained by using Pt-Pt10%Rh thermocouple. Above 1900 K, the heater powers required to initiate melting in Al_2O_3, Y_2O_3, and TiB_2 and decomposition of α- SiC were used.

mediate soft phase processing (ISPP). Sintered compacts of SiC, TiB_2, TiB_2-TiC, TiB_2-TiC-SiC, NiAl, NiAl-TiB_2 with ~99% of the theoretical density were obtained by using above processing techniques.

2. EXPERIMENTAL

The HPS, HPCS and HPRS experiments were carried out in a 200-ton cubic anvil apparatus (anvil face 10 mm square) capable of generating pressures up to 6.5 GPa and temperatures up to 3300 K. The high-pressure high temperature cell used in these experiments is shown in Fig.1. This cell was developed in the laboratory to suit the synthesis experiments. The details of the cell are reported elsewhere [1]. The oil pressure specimen pressure relation was obtained using the Bi I $\rightarrow$ II (2.55 GPa) and Yb fcc $\rightarrow$ bcc (4.0 GPa) transformations. The heater power versus temperature calibration curve was established using Pt-Pt10%Rh thermocouple up to 1900 K. For calibration above 1900 K, the heater powers required to initiate melting in Al_2O_3, Y_2O_3, and TiB_2 and decomposition of α-SiC were determined. The melting (or decomposition) of the specimens was detected by examining the microstructure of the specimens recovered after pressure-temperature treatment. The temperatures estimated at various heater power inputs are shown in Fig.2.

The powder mixtures were prepared by ball milling in hexane medium for 24h (Fritsch Pulverisette-5 centrifugal mill). The milled powder mixtures were dried and degassed at 700 K under vacuum (10^{-4} Torr) for 2h, before conducting the synthesis experiments. The powder sample was packed in the tubular graphite heater (Fig.1) and pressurized to the desired value. Once the required pressure was attained, the sample was heated by passing current through the graphite heater. The heating rate was $40^0 K\ s^{-1}$. After the

dwell time, the heater power was turned off and the sample was allowed to cool slowly under pressure. When the sample temperature reached around 500 K, the pressure was released and the sample was recovered for further study. The typical dimensions of the recovered samples were ~3.5 mm in diameter and 4 mm in thickness.

The RHP and ISPP experiments were carried out in a hot press fabricated in the laboratory [2]. The powder mixture was cold compacted at 400 MPa into a cylindrical compact of 13 mm diameter and 8 mm height. These compacts, with green density 55 to 66% of theoretical density (TD), were placed in a graphite die and a load corresponding to pressure of 20-45 MPa was applied. The heating was done by an induction furnace. The heating rate was $15^0 K\ s^{-1}$.

The surfaces of the sintered samples were flattened by wet polishing on a cast iron wheel using diamond paste of 50μm grit size. This was followed by fine polishing with diamond paste of decreasing grit size (25, 5, 1μm). The different phases in the sintered compacts were identified by x-ray diffraction using Cu K_α radiation of wavelength 1.542 Å . The density was measured by volume displacement method. The microstructural observations were carried out in optical (Neophot 2) and JEOL 840A scanning electron microscope (SEM). Shimadzu HSV 20 microhardness tester with a load of 1.96 N was used to determine the hardness. For indentation fracture toughness determination, a load of 49 N was used. The fracture toughness was calculated from the equation [3]

$$K_{IC} = 0.0824\ (P/C^{3/2})$$

Where, P is the indentation load (N) and C the crack length (μm). Ten indentations were made on each sample for hardness and fracture toughness measurements, and the average values were reported.

3. RESULTS AND DISCUSSION

3.1 High pressure sintering (HPS)

In general, ceramic materials with high degree of covalent bonding have excellent high temperature properties. Pure crystalline solids containing chemical bonds, which are primarily covalent, are unsinterable, meaning that no extensive macroscopic shrinkage (densification) of the powder compact occurs during pressureless sintering. It is believed that in these solids the bulk diffusion is slow even at high temperatures resulting in very little material transport to the pore surfaces. Therefore, the addition of a second phase becomes inevitable to promote densification. The hot pressing by conventional methods usually results in poorly bonded friable compacts, which show fractional improvement in density nearly equivalent to that, obtained by cold compaction. Application of pressure during sintering helps in densification, but the magnitude of the applied pressure necessary to obtain compacts with near full density is rather high (of the order of few GPa).

3.1.1Silicon carbide [4] : The SiC powder used in the study was supplied by Grindwell Norton. The x-ray diffraction analysis indicated that the powder contained 6H (~45%), 4H (~18%), 15R (~17%) and β-SiC (~20%) phases. The average particle size was about 5μm. The sintering experiments were carried out at a temperature of 2073 K in the pressure range 1.7-3.0 GPa. The sintering time was between 5-30 min.

The application of high pressure initially causes densification by particle rearrangement. The stress distribution at this stage is very uneven, being very high in the regions where the grains are in direct contact, and virtually zero in the non-contact regions. The pressure

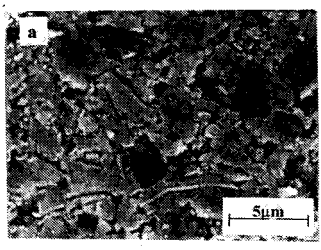


Fig.3. Scanning electron micrographs of SiC compacts prepared by HPS. The HPS was carried out at 2 GPa and 2073 K for (a) 5 min and (b) 30 min. The microstructures contain equiaxed grains of SiC. The SiC grain growth due to increase in sintering time can be seen.

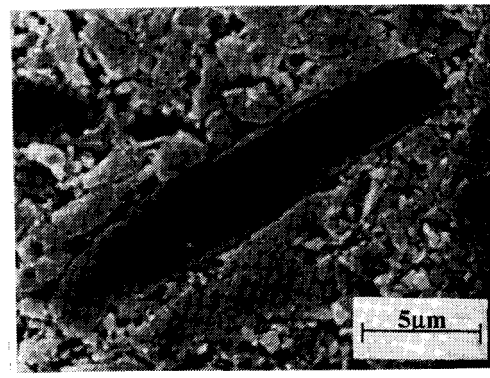


Fig.4. Scanning electron micrograph of SiC compact prepared by HPS. The HPS was carried out at 3 GPa and 2073 K for 30 min. The microstructure contains α-SiC grains with high aspect ratio. This characteristic microstructural feature is known to develop [5] when β-SiC transforms to α-SiC.

at the point of contacts is much more than the average stresses (1.7-3.0 GPa) over the whole compact. The stresses at the contact points exceed the fracture stress of brittle solid particles like SiC. Therefore, the communition of the SiC particles and the concomitant rearrangement of particles result in the densification of the starting material during the compaction process. Each particle in this network is constrained to be in contact with several neighbouring particles. For further densification, the whole network has to deform plastically.

On raising the temperature, due to surface diffusion, smoothening of particle surface takes place. This results in particle rearrangement leading to further densification. In addition, the deformation of particles at elevated temperatures become operative. In covalently bonded solids like SiC, the intrinsic diffusivity is very low and, therefore, the Peierls stress is high for the movement of dislocation. Hence, a higher pressure of the order of 2-3 GPa is required for complete densification. A small amount of porosity (<1%) is always present in all the HPS compacts. This is mainly due to the adsorbed gases on the raw material particle surfaces. During sintering, they get released but can not escape from the high-pressure cell and leads to sintered porosity. All the compacts sintered at 2073 K in the pressure range 1.7-3.0 GPa for 5-30 min had density > 99% of TD. There was no pressure dependence on the sintered density.

Some typical microstructures of the SiC compacts are shown in Fig.3. The microstructure contains mainly equiaxed α-SiC grains. The average grain size is about 2μm, which is much less than that of the starting particle size (5μm). This indicates the extent of cold crushing during compaction. It is also evident from the microstructure that particles, which have nearly straight surfaces, align themselves to establish the contact over a large surface area with the neighbouring particles.

The x-ray diffraction studies showed that the HPS compacts contained predominantly 6H α-SiC. Most of the β-SiC that was present in the starting material has transformed to α-phase. At higher temperatures, the β-SiC transforms readily to α-SiC with a characteristic microstructural feature. Normally, the transformed α-SiC grains are found to

Table I. Properties of TiB_2 and TiB_2-TiC compacts prepared by HPS at different temperatures. The HPS was carried out at 3 GPa for 5 min. X is the mean value, σ the standard deviation and %TD the percent theoretical density.

Composition	Temperature (K)	Density (%TD) X (σ)	Hardness (GPa) X (σ)	Fracture toughness MPa$\sqrt{m}$ X (σ)
TiB_2	2250	94.63 (0.12)	19.2 (1.2)	-
TiB_2	2500	97.11 (0.15)	21.7 (1.5)	2.8 (0.2)
TiB_2	2750	97.95 (0.13)	24.5 (0.8)	3.2 (0.1)
TiB_2-15vol%TiC	2250	98.21 (0.09)	22.6 (1.3)	3.5 (0.3)

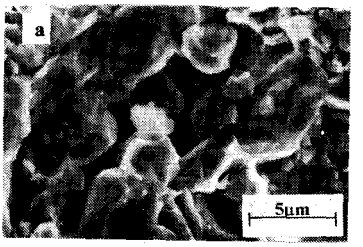


Fig.5. Scanning electron fractographs of TiB_2 compacts prepared by HPS. The HPS was carried out at 3 GPa and (a) 2250 K and (b) 2750 K for 5 min. The microstructures contain equiaxed grains of TiB_2. The grain growth due to increase in sintering temperature can be seen.

be elongated with high aspect ratio (plate- or feathery-like morphology [5]. The plate-like SiC grains observed in the micrograph (Fig.4) is because of $\beta \rightarrow \alpha$ transformation.

The hardness values of the HPS compacts are in the range 26.7- 33.5 GPa as against 27 GPa reported for fully dense α-SiC. The hardness values are lower for compacts sintered at 1.7 GPa than those sintered at 2.0 GPa or 3.0 GPa. The reason could be that though 1.7 GPa pressure is sufficient enough to yield full density, but not enough to provide strong bonding between SiC particles. The indentation fracture toughness values obtained are in the range 3.5-3.7 MPa$\sqrt{m}$.

3.1.2 Titanium diboride and its composites [6]: The TiB_2 (9.5μm) and TiC (8.3μm) powders used for the study were supplied by HC Starck, Germany and Triebacher Chemische Werke, Austria respectively. The HPS experiments were carried out at 3 GPa in the temperature range 2250-2750 K for 5 min.

The measured densities (as a percentage of TD) of the sintered TiB_2 compacts are listed in Table I. The density of the sintered compacts increases monotonically with the increase in sintering temperature. To obtain compacts with 98% density, sintering temperature as high as 2750 K is required. The densification mechanisms during HPS of TiB_2 are same as those described earlier in case of SiC. However, with the increase in temperature, the diffusion as well as the deformation are enhanced resulting in better densification.

The microstructures of the TiB_2 compacts sintered at different temperatures are shown in Fig.5. The microstructures contain equiaxed grains of TiB_2. The grain size of TiB_2 is found to increase with the increase in sintering temperature. The hardness and fracture toughness values are listed in Table I. Though there is improvement in the hardness values with the increase in density, virtually no change is observed in the fracture toughness values. Appreciable grain growth is observed in the compacts sintered at higher temperatures (Fig.5). This has adverse effects on the fracture toughness.

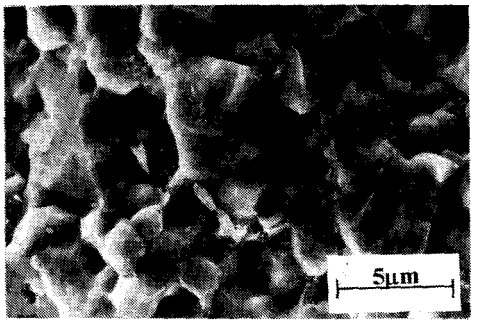


Fig. 6. Scanning electron fractograph of TiB_2-TiC compact prepared by HPS. The HPS was carried out at 3 GPa and 2250 K for 5 min. The microstructure contains equiaxed grains of TiB_2 and TiC.

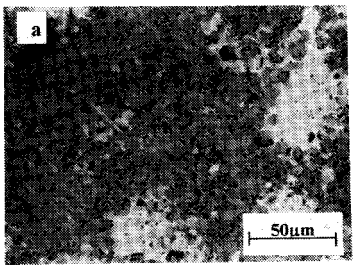
Therefore, the beneficial effect of high density has been nullified due to exaggerated grain growth in the material.

The combination of TiB_2 and TiC is thermodynamically stable up to 2700 K, undergoing a quasibinary eutectic reaction in the temperature range 1900-2000 K[7]. For compositions other than eutectic composition, the eutectic liquid formed at the TiB_2 and TiC particles is transient in nature. Since the eutectic liquid has a very good wettability with both TiB_2 and TiC, it spreads over the solid particle surfaces soon after its formation due to surface tension. Under the applied pressure, the liquid phase is squeezed into the voids. With time, the composition of the liquid shifts from the eutectic composition and the liquid solidifies. Concurrently, the solubility of the solid in the liquid results in surface smoothening which aids in the rearrangement of the particles for closer packing and pore elimination. The formation of liquid phase also reduces the sintering temperature required to obtain dense compacts. For example, the sintering temperatures for obtaining TiB_2 and TiB_2-15mol% TiC compacts with 98% density are 2750 and 2250 K respectively (Table I). The composite compacts have uniform and finer microstructures than those of monolithic compacts (Figs. 5 and 6).

3.2 High pressure self-combustion synthesis

A more elegant method to overcome the problems in sintering of ceramic powders is combustion synthesis, where the microstructures can be tailored in a much controlled fashion. This process, commonly known as self-propagating high temperature synthesis (SHS), has been used extensively to synthesize a large number of compounds. The SHS process has two distinct advantages. As the heat of reaction is used to complete the reaction, considerable heat energy savings are expected. The reaction product is free from volatile impurities as these are driven out when the reaction zone reaches very high temperature. The reaction product, however, is porous. The porosity is caused by a number of factors, such as, the volume change inherent in the reaction, short duration (insufficient for sintering) of the high temperature reaction zone, porosity present in the reaction mixture, and escape of the gases during the reaction. For any practical application, the product of SHS has to be compacted and sintered. Both synthesis and compaction can be achieved in a single step if the SHS is carried out under pressure. This process is commonly termed [9] as high-pressure self-combustion synthesis (HPCS).

3.2.1Silicon carbide [10-13] : Silicon powder (99.999% pure from Koch-Light Ltd., UK) and amorphous carbon powders from three different sources: Philips carbon black, soot collected by burning camphor, and activated charcoal, GR grade marketed by Sarabhai Chemicals, India were used as the starting material. The carbon powders were heated to 1700 K under inert atmosphere for 2h to remove the volatile matter. The reactant mixtures with Si: C molar ratios 1 : 1, 1 : 1.02 and 1 : 1.05 were prepared by both dry and wet milling in hexane medium. HPCS experiments were carried out at 3 GPa in the temperature range 2100-2900 K. Two types of heating schedules were adopted: (i) heating to desired temperature (one-step heating) and (ii) holding the temperature at 1500 K for 10 min followed by heating to desired temperature (two-step heating).



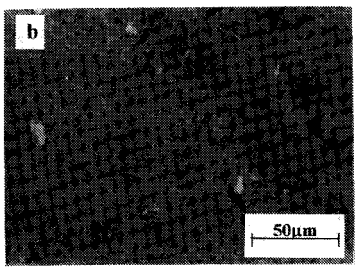


Fig.7. Optical micrograph of SiC compacts obtained by HPCS from (a) dry milled and (b) wet milled reactant powders. The HPCS was carried out at 3 GPa and 2500 K for 5 min. The SiC (grey), Si (white) and C (black) phases are seen. The efficiency of reaction is better with wet milled powder.

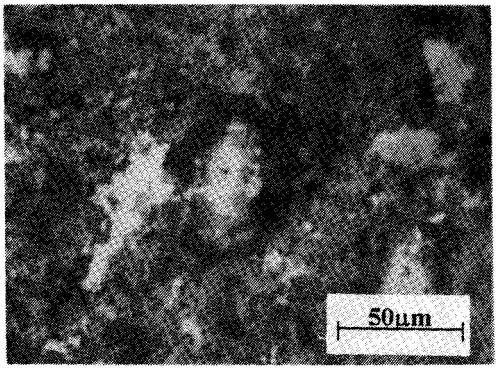


Fig.8. Optical micrograph of SiC compact obtained by HPCS. The HPCS was carried out at 3 GPa and 2300 K for 1 min. The microstructure contains large volume fraction of unreacted Si (white).

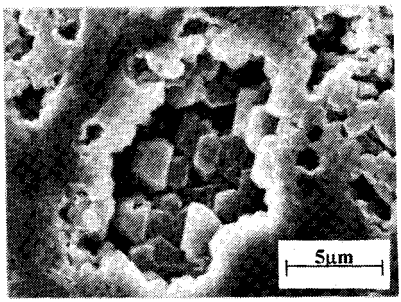
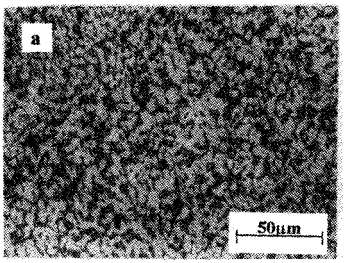
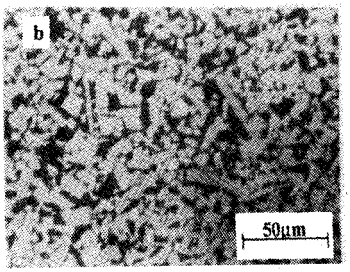


Fig.9. Scanning electron microstructure of SiC compact showing the growth of SiC crystals in the molten Si pool. The unreacted Si has been removed by etching with HF acid.

The reactivity in the Si - C reaction is dependent on the crystallinity of the carbon powder. Among the three types of carbon powder, activated charcoal results in better reactivity. X-ray diffraction analysis has shown that this carbon powder is having least crystallinity. Analysis of the dry and wet milled powder mixtures has shown that the wet milled powder has finer particle size and narrower particle size distribution. Microstructures of the compacts prepared from these two types of reactant mixtures are shown in Fig.7 Three distinct phases namely, white (Si), gray (SiC), and black (unreacted carbon) can be seen in the microstructure. The phases were identified by hardness measurements as well as by metallographic observations. The results indicate that the formation of SiC is facilitated by fine particle size and narrow size distribution in the powder mixture. Due to the presence of oxygen (either adsorbed or combined), some amount of carbon is lost during reaction, and is not available for the Si - C reaction. This results in certain amount of free silicon in the sintered compacts. In the present set of experiments, it was estimated that about 5% excess carbon would be required to avoid free silicon in the compacts. Keeping the above things in view, further experiments were carried out with wet milled reactant mixture of silicon and activated charcoal with Si: C molar ratio of 1:1.05.

The microstructure of the compact prepared at 2300 K for 60s is shown in Fig.8. This contains large fraction of unreacted silicon and carbon. The heat of formation of SiC is relatively low (69kJ/mol) and is insufficient for the spontaneous propagation of the reaction. Also, the application of high pressure establishes good contact between the reactants leading to enhanced heat loss by conduction. Therefore, if the reactant mixture is ignited, with no further supply of energy, the reaction progresses through the whole compact but is limited to the surfaces of the reactants. At the start of the reaction, silicon





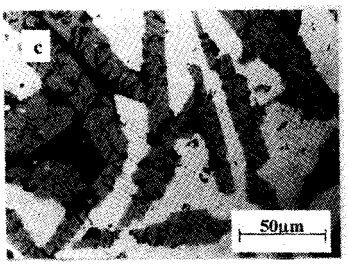


Fig.10.Optical micrograph of SiC compacts prepared by HPCS. The HPCS was conducted at 3 GPa and (a) 2300 K, (b) 2500 K and (c) 2900 K for 5 min. The microstructural evolution at different HPCS temperatures are seen. At 2300 K, the microstructure contains equiaxed β-SiC. Increase in synthesis temperature results in β→α transformation (~2500 K) and decomposition of α-SiC to Si and C (~2800 K).

melts and reacts with solid carbon. Initially, several nuclei of SiC form at the Si-C interface, which with time, grow and impinge on each other. Thus, a solid SiC rim is formed around the molten silicon pool and physically separates the reactants. A typical microstructure showing the growth of SiC into silicon melt is shown in Fig.9. For the reaction to proceed, carbon atoms have to diffuse through the grain boundaries in this SiC layer. Since the diffusion coefficient of carbon in SiC is low, it is essential to maintain high temperature until the reaction is completed. The results clearly indicate that the reaction in the HPCS of SiC takes place in two steps. After ignition of the reaction mixture, the reaction is self-propagating but limited to the surfaces of the reactants. On subsequent holding at high temperatures, the reaction is completed by the diffusion of carbon through SiC. The time required for the completion of the reaction is dependent on the synthesis temperature as well as the particle size in the reactant mixture.

In the reaction synthesis of SiC, carbon reacts with molten silicon and generally forms β-SiC (Fig.10a). Typically, the microstructure exhibits equiaxed grains of β-phase. At temperatures 2500 K, the microstructure changes to a mixture of equiaxed (β-SiC) and elongated grains (α-SiC). The elongated grains with high aspect ratio (plate-like morphology) are known to develop when β-SiC transforms to α-SiC (Fig.10b). This indicates that initially molten silicon reacts with carbon to form β-SiC which transforms to α-SiC at temperatures ~2500 K. The β → α transformation is complete at 2500 K in about 5 min. Further increase in temperature or synthesis time results in coarsening of α-SiC. Around 2800 K, the decomposition of α-SiC to silicon and carbon is observed (Fig.10c). Above this temperature, the microstructure contains α-SiC platelets, silicon, and carbon.

The densities of the compacts prepared at various processing conditions are listed in Table II. The porosity in the sintered compacts is less when the heating is done in two steps. The porosity in the sintered compacts is due to the release of adsorbed gases and gaseous products at high temperatures. In pressureless sintering, most of these gaseous phases come out of the sample. In high pressure sintering, the compact is completely isolated from the atmosphere and, therefore, no gaseous phase can escape. The amount of gaseous products as well as the gas pressure inside the pores increases with the increase in temperature. Both these factors hinder densification and result in higher porosity in the sintered compacts. When the temperature is held at 1500 K for 10 min, the

Table II. Properties of SiC compacts prepared by HPCS at different temperatures. Ths HPCS was carried out at 3 GPa for 5 min. %TD is the theoretical density. I and II denote, respectively, the one-step and two-step heating schedules.

Reactant powder (Si : C molar ratio)	Temperature (K)	density, g/cm^3 (% TD)	
		I	II
1 : 1.02	2100	3.13 (96.4)	3.18 (97.8)
1 : 1.02	2500	2.87 (88.5)	3.15 (97.1)
1 : 1.05	2100	3.12 (96.0)	3.21 (98.8)

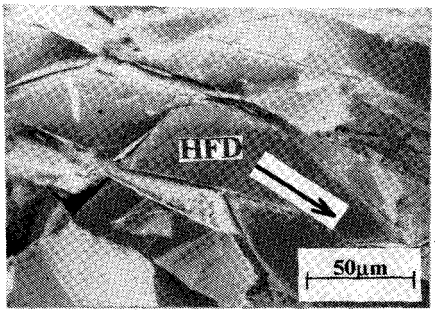


Fig.11. Scanning electron fractograph of TiB_2 compacts obtained by igniting the Ti-B mixture at 3200 K under 3 GPa pressure. Faceted TiB_2 grains grown preferentially along the heat flow direction (HFD) are seen

reactant mixture gets densified due to deformation of silicon particles. This hinders the evolution of gaseous products at higher temperatures and results in denser products.

The hardness value of the compacts synthesized in the temperature range 2100 2500 K (β-SiC) is ~23 GPa. Compacts synthesized in the temperature range 2500-2700 K have hardness of ~30 GPa in the α-SiC regions. Irrespective of the heating schedule (one-step or two-step), the compacts have similar hardness.

3.2.2 Titanium diboride and its composites [6]: The titanium (13μm) and the amorphous boron (15μm) powders used in these experiments were obtained from SPMS Powder Met., France and BARC, India respectively. The powder mixtures corresponding to the compositions TiB_2 and TiB_2-15 mol% TiC were prepared by wet ball milling. The HPCS experiments were carried out at 3 GPa in the temperature range 2250-2750 K. The desired temperature was reached in about 5s and maintained for 5 min. In few experiments, the heater power was switched off after 5s heating period. The temperature thus attained is referred to as ignition temperature. After the ignition, the temperature is maximum at the reaction zone (adiabatic temperature), whereas in the other part of the compact, the temperature (sample temperature) is much less due to heat losses by conduction through the WC anvils of the press.

The exothermicity of the reaction forming TiB_2 is very high (300 kJ/mol) compared to 69 kJ/mol in case of SiC. From the calculations, it has been shown that an adiabatic temperature of ~4000 K can be attained in the Ti+B reaction [14]. This temperature is in excess of the melting point of TiB_2 (3173 K). If the reaction mixture is ignited at very high temperatures, the reaction product (TiB_2) melts and solidifies into a sintered mass during cooling. These microstructures are typical of cast structures in which the grains are elongated in the heat flow direction. Such a microstructure obtained in the TiB_2 compact synthesized by igniting the reactant mixture at 3200 K is shown in Fig.11. Since the sample temperature is above the melting point of the product TiB_2 phase, it becomes very difficult to have a control over the microstructure. These compacts have very poor fracture toughness (1.8 MPa$\sqrt{m}$), mainly because of the large grains. Therefore, it is important to choose the ignition temperature such that the sample temperature is always below the melting point of the product phase.

A minimum ignition temperature of 2250 K is required to make the reaction self-sustaining in both Ti-B and Ti-B-C systems. Below this temperature, the reaction is incomplete, and

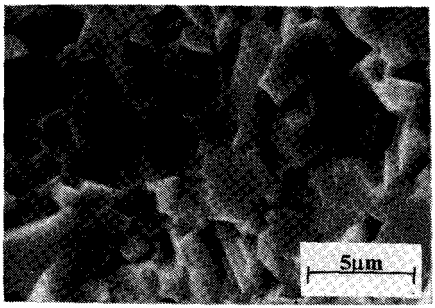


Fig.12. Scanning electron fractograph of TiB_2-TiC compacts obtained by igniting Ti-B-C mixture at 2250 K under 3 GPa pressure. The microstructure contains randomly oriented equiaxed grains of TiB_2 and TiC.

the compacts contain elemental reactants and substoichiometric product phases. The microstructures consist of randomly oriented TiB_2 and TiC grains (Fig.12).

During heating above 1940 K, titanium melts and the liquid phase thus produced comes in contact with solid boron and carbon particles. Because of the high exothermicity of the Ti-B reaction, the reaction propagates rapidly giving rise to TiB_2 as the product phase. However, in case of Ti-C reaction, the product is substoichiometric at the initial stage. Transportation of reactants through TiC_x is required for the reaction to proceed. The diffusion coefficients of B and C in TiC_x are about three times larger [15] than that of titanium in TiC_x. Therefore, diffusion of B and C through the reaction products is the primary process for the transport of the reactants. The boron that diffuses in, reacts with the excess titanium in the substoichiometric carbide to produce TiB_2 resulting in the increase in carbon-to-metal ratio, x, in TiC_x. The TiC_x layer formed at the initial stage, dissolves in the liquid titanium and precipitates out as TiC. The concentration gradient in the TiC_x layer provides the driving force for the diffusion of C through it. In the titanium melt, TiC is formed by the crystallization due to supersaturation and, subsequent growth of the nuclei leads to the formation of sintered grain structure [15]. Efforts were made to establish the possible reaction sequence in Ti-B-C system during HPCS. Compacts with incomplete reaction were produced by igniting the reactant mixture at 2250 K. These compacts were characterized by x-ray diffraction study, and microstructural study. Also, nano-hardness measurements were performed on the individual phases to determine the composition of TiB_2 and TiC_x phases. Based on the results, the following sequence of reaction in Ti-B-C system is proposed: (a) titanium reacts with boron to form TiB_2, (b) titanium reacts with carbon to form titanium rich TiC_x (steps a and b can occur simultaneously), (c) boron reacts with TiC_x to form TiB_2, resulting in an increase of C/Ti ratio in TiC_x, and finally (d) carbon reacts with TiC_x to form stoichiometric TiC. A detailed report on this study can be found elsewhere [6].

It is interesting to compare the results of the experiments with 5 min holding time with those with no holding, i.e., when the heater power was switched off after the end of the heating period (Table III). Although the reaction was complete in both the cases, there was improvement in the density when the temperature was maintained for 5 min. During heating, when titanium melts, the compact densifies almost completely. As the reaction proceeds, the solid reaction products form with a net decrease in volume. At the later stage of the reaction, the compact attains rigidity due to large volume fraction of the solid phase, and further densification slows down significantly. If the temperature is maintained at this stage, the rigid structure of the product phases deforms resulting in further densification. The density, hardness and fracture toughness values as a function of composition and processing parameters are listed in Table III.

Table III. Properties of TiB_2 and TiB_2-TiC compacts prepared by HPCS at different temperatures. The HPCS was carried out at 3 GPa pressure. X is the mean value, σ the standard deviation and %TD the percent theoretical density.

Composition	Temperature (K)	Time (min)	Density (%TD) X (σ)	Hardness (GPa) X (σ)	Fracture toughness (MPa√m) X (σ)
Ti + B (TiB_2)	2250	NH*	97.82 (0.12)	23.6 (1.5)	3.5 (0.4)
	2500	NH	98.04 (0.07)	24.0 (1.2)	3.8 (0.2)
	2250	5	98.72 (0.13)	24.2 (0.6)	3.9 (0.3)
	2500	5	98.86 (0.17)	24.5 (1.1)	3.8 (0.2)
Ti + B + C (TiB_2-15vol%TiC)	2250	NH	98.53 (0.08)	22.7 (1.4)	4.3 (0.2)
	2250	5	99.14 (0.10)	23.8 (0.7)	4.2 (0.2)
	2500	5	99.03 (1.0)	23.5 (1.0)	4.6 (0.3)

** No holding*

Table IV. Properties of NiAl and TiB_2-NiAl composites fabricated by HPRS and RHP. X is the mean value, σ is the standard deviation and %TD the percent theoretical density.

Sample	Synthesis temperature (K), time (min)	Density (%TD)	Hardness (H_v)(GPa) X (σ)	Fracture toughness (MPa√m) X(σ)
NiAl (HPRS)				
1	1173, 15	99.3	5.4 (0.3)	-
2 (annealed)	1173, 15	97.5	4.0 (0.3)	-
TiB_2-30vol%NiAl (HPRS)				
3	1173, 30	99.0	13.2 (0.6)	5.69 (0.60)
4	1173, 30	98.8	12.8 (0.6)	5.53 (0.28)
TiB_2-30vol%NiAl (RHP)				
5	1923, 1	90	-	-
6	1923, 15	100	15.0 (1.2)	3.82 (0.31)
TiB_2-10vol%NiAl (RHP)				
7	1923, 30	100	22.1 (1.2)	2.97 (0.28)

temperature generation during reaction is relatively less. In unavoidable systems, where the reactions are highly exothermic, certain diluents are added to the reactant mixtures for reducing the overall heat generation. In reaction synthesis and sintering, the reaction is allowed to proceed slowly so that a better control over the microstructures can be achieved.

3.3.1Nickel aluminide [16] : Nickel (3.7 μm) and aluminium (16.5 μm) powders used in these experiments were supplied by INCO, UK and ALCOA respectively. The experiments were carried out at 3 GPa pressure and 1173 K for 15 min.

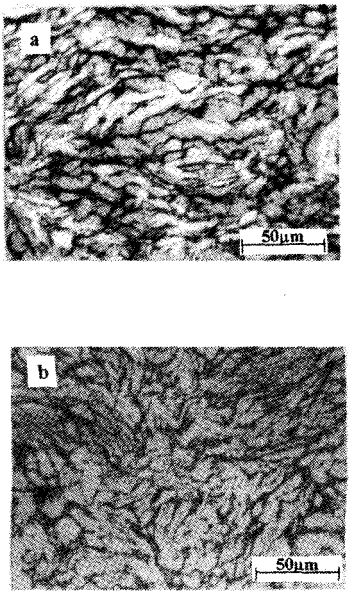


Fig. 13. Optical micrograph of NiAl : (a) HPRS (b) HPRS followed by annealing at 1373 K for 120 min. The HPRS was conducted at 3 GPa and 1173 K for 30 min. In (a) the gray phase is Ni_3Al and white phases are NiAl and Ni_2Al_3. After annealing, the microstructure is uniform confirming a single phase material.

During HPRS, the exothermic reaction between Ni and Al generates enough heat to produce a liquid phase. This liquid provides a faster diffusion than encountered in the solid state leading to enhanced densification. The amount of liquid phase formed depends on the powder composition (Al content) and temperature. The stoichiometric Ni-Al composition can produce as much as 50 vol% liquid [17] in the temperature range 873-973 K. The application of pressure during reaction sintering helps in eliminating the big pores often observed in the pressureless sintering. A pressure of 100 MPa is sufficient to obtain NiAl compacts with 99.9% density [18]. However, in HPRS certain amount of porosity is unavoidable due to the entrapment of adsorbed and volatile gases in the high pressure cell (Table IV). These are closed porosity, and if the sintered compacts are annealed at higher temperatures, the size of these pores enlarges. The NiAl compacts synthesized at 1173 K contain NiAl, Ni_2Al_3 and Ni_3Al phases. These phases can easily be identified by etching the polished specimen with Kallings solution-2. (Fig.13). The reaction sinter of NiAl consists of complex reaction with several sequential steps. First the Al-rich compounds $NiAl_3$ and Ni_2Al_3 are formed. Subsequently, these phases react with Ni to form NiAl. Depending on the availability of Ni in the vicinity of NiAl, Ni_3Al can also form [19]. Therefore, in a reaction sintered compact where the reaction is incomplete, all the four intermetallic phases are likely to be present. In HPRS, the heat loss in the reaction zone by conduction is high leading to incomplete reaction. The reaction is completed when these compacts are annealed at 1373 K for 120 min (Fig.13).

3.3.2 Titanium diboride - Nickel aluminide composite [16] : The TiB_2- NiAl composites containing 10-30 vol% NiAl were prepared at 3 GPa pressure and 1173 K. The synthesis time was between 15-45 min. A master alloy powder mixture of Ni-50 at% Al was prepared first, which was used to prepare the composite powder mixtures of desired compositions.

The densification mechanism in TiB_2-NiAl composites is different from that in pure NiAl. The major volume fraction in these composites is TiB_2 phase (70-90 vol%). During pressurization, the densification takes place by the rearrangement of the TiB_2 particles. The yield strength Ni and Al being very low as compared to that of TiB_2, these ductile phases deform significantly and fill the voids. On raising the temperature, the reaction starts and the liquid phase is formed. The volume fraction of the liquid phase decreases with the progress of the reaction. Finally, the liquid disappears when the reaction is complete. However, presence of the liquid even for a short period is beneficial for densification, as second stage of particle rearrangement takes place during this period. In the TiB_2-NiAl composite, the volume fraction of liquid phase and the heat generated due

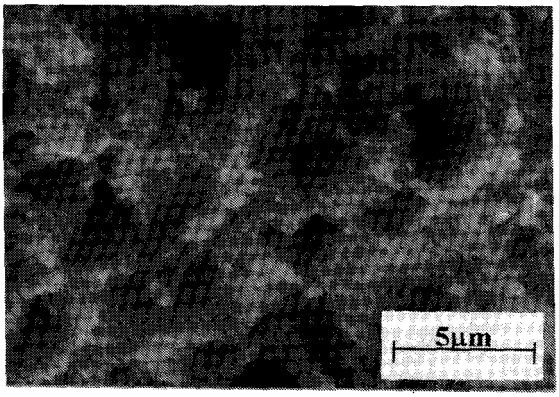


Fig. 14. Scanning electron fractograph of TiB_2- 30vol% NiAl obtained by HPRS. The HPRS was carried out at 3 GPa and 1173 K for 30 min. The micro- structure contains TiB_2 grains embedded in the NiAl matrix.

to reaction are less compared to pure NiAl. As a consequence, the time required for densification is longer. When the volume fraction of the matrix phase is low, the liquid phase is not sufficient to fill all the pores and often results in sintered porosity (Table IV).

The x-ray diffraction study has shown that the composite compacts contain mainly TiB_2, NiAl and Ni_3Al. After annealing at 1373 K for 2h, the Ni_3Al phase disappears. The microstructures consist of TiB_2 grains embedded in the NiAl matrix (Fig.14). Due to the low synthesis temperature, the problem of grain growth in TiB_2 phase is not encountered in HPRS. Increase in sintering time results in a better bonding between the matrix and the TiB_2 phases leading to the improvement in mechanical properties. Annealing treatment eliminates the brittle Ni_2Al_3 phase in the HPRS compacts and results in enhancement of the fracture toughness property. Annealing also leads to homogenization of the matrix phase, which results in more uniformity in the mechanical properties.

TiB_2-NiAl composites were also produced by reactive hot pressing (RHP) at 1923 K in the pressure range 20-45 MPa. The hot pressing time was between 1-30 min. The reaction between the reactant phases is completed even within 1 min, but the compacts contain substantial amount of porosity (Table IV). Fully dense compacts can be obtained only when the hot pressing temperature is maintained for some time. The RHP temperature (1923 K) is higher than the melting points of all the intermetallics in the Ni-Al system. This results in the formation of a liquid phase, and the densification proceeds through liquid phase sintering. The time required for complete densification depends on the volume fraction of the liquid phase. It increases with the decrease in the volume fraction of the liquid phase forming additives.

In addition to the phases present in the HPRS compacts, some additional phases (Ni_2B, AlB_2 and $NiTi_2$) are formed in the RHP composites. The liquid phase in the RHP stays in the compact for longer duration (15-45 min). This enhances the reaction between TiB_2 and the matrix phase giving rise to borides of Ni and Al. The volume fraction of these phases increases with the increase in the hot pressing temperature and time. These phases are formed at the cost of NiAl and are very brittle. As a result, the RHP composites have superior hardness but inferior fracture toughness as compared to those for HPRS composites. Therefore, careful selection of the temperature and time has to be exercised so that the formation of these brittle phases is minimum. Since the liquid phase is readily available in RHP, the grain growth in the TiB_2 phase takes place mainly by solution reprecipitation (Fig.15). In contrast, in HPRS, due to nonavailability of the liquid phase and low synthesis temperature, almost no grain growth takes place in the TiB_2 phase.

3.4 Ceramic-ceramic composites by intermediate soft phase processing [20-21]

A process has been developed to fabricate ceramic-ceramic composites with high density at relatively low temperatures and pressures through the formation of an intermediate soft phase. The principle of the method is as follows: The starting materials in powder form are

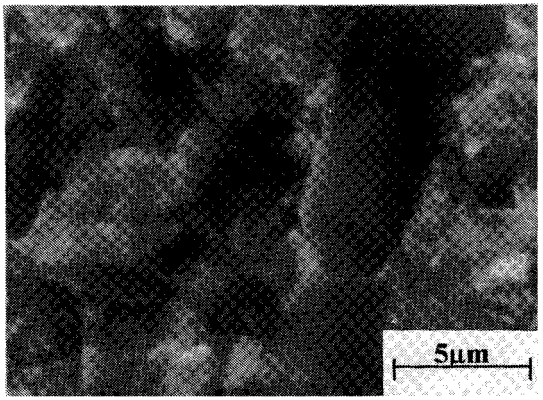


Fig. 15. Scanning elecron fractograph of TiB_2- 15vol% NiAl produced by RHP at 20 MPa and 1873 K for 30 min. Grain growth in the TiB_2 phase can be seen.

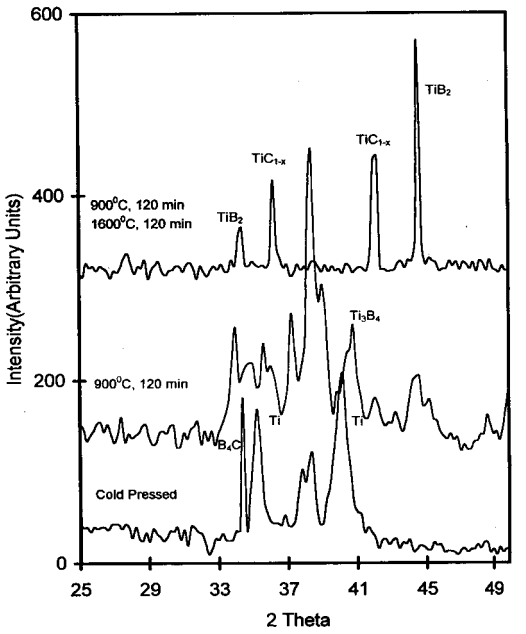


Fig.16. The x-ray diffraction pattern of the starting powder (Ti:B_4C = 4:1) and the compacts obtained after 1st and 2nd stages of ISPP. The processing are also indicated.

mixed and cold pressed. The cold pessed compacts are subjected to hot pressing in two steps. One of the constituents in the mixture forms a non-stoichiometric soft phase at relatively low temperature (< 0.6 T_m). The other constituent is the reactant phase, which reacts with the soft phase at higher temperatures to form hard matrix and reinforcement phase. The processing temperature is well below the melting point of the individual components of the composite. The pressure required is slightly above the yield point of the intermediate soft phase.

Using the above technique TiB_2-TiC composites were prepared from the powder mixture of Ti and B_4C. Titanium (13 μm, 99% purity, ESK, Germany), and boron carbide (10 μm, 98% purity, SPMS-Powder Met., France) were used as the starting materials. Two types of powder mixtures with Ti:B_4C molar ratios of 4:1 and 3:1 were prepared to obtain composites of different compositions. The synthesis experiments were carried out in two steps (1173 and 1873 K) in the pressure range 20-45 MPa.

The x-ray diffraction study of the compacts after the first step of hot pressing has indicated that Ti and B_4C reacts to form a number of phases. Most of these phases are substoichiometric. A typical x-ray diffractogram recorded for the composition Ti:B_4C=4:1 is shown in Fig.16. It can be noted that a large volume fraction of the compact contains substoichiometric TiC_x. The yield strength of TiC_x is a function of composition, the yield strength increases with the increase in the C to metal ratio. At the beginning of the reaction, the value of x is very close to 0.66. At 1173 K, the $TiC_{0.66}$ can plastically deform under relatively low pressure (45-80 MPa). Holding at this temperature for reasonable time results in compacts with better than 90% density. However, at the end of this step of processing, the reaction is not complete and the compacts contain various intermediate phases. In fact, the reaction is not allowed to complete so that the intermediate soft phases persist for a long time and thereby a better densification is achieved.

In the second step of processing, the temperature is raised to 1873 K. The heating is done at a slow rate so that the reaction proceeds slowly. The advantage of the low yield point of the substoichiometric phases is used for densification. Otherwise, once the reaction is complete, high pressures and temperatures are required to eliminate the remaining porosity. After reaching 1873K, the temperature is maintained for some time.

Table V. Properties of TiB_2-TiC composites fabricated by intermediate soft phase processing.

Composition	Step I (1173 K)		Step II (1873 K)		Density (% TD)	Hardness (GPa)	Fracture toughness (MPa √m)
	Pressure (MPa)	Time (min.)	Presuure (MPa)	Time (min.)			
Ti : B_4C (4 : 1)	20	120	20	240	96	20.7	-
	45	60	45	120	98	22.8	-
Ti : B_4C (3 : 1)	45	45	45	120	99	23.5	4.0

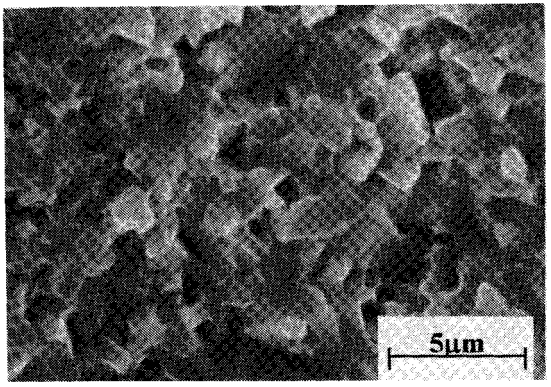


Fig.17. Scanning electron fractograph of TiB_2-TiC composite processed by ISPP. The microstructure contains equiaxed grains of TiB_2 and TiC.

During this time, the soft phase (TiC_x) reacts with the reactant phase (B_4C) to form the hard matrix and the reinforcement phases. If the stoichiometric composition of TiB_2-TiC composite is chosen, the value of x in TiC_x reaches 1.0 at the end of the reaction, whereas various phases of Ti-B compound adjust their composition to stoichiometric TiB_2. The microstructure consists of TiB_2 and TiC grains (Fig.17). A range of composites can be obtained by choosing various Ti:B_4C molar ratios in the starting powder mixture. Some important properties of these composites are presented in Table V.

4. CONCLUSIONS

It has been demonstrated that a large number of monolithic and composite ceramics with high density can be fabricated by high pressure and high temperature synthesis and sintering. Application of high pressure is beneficial in obtaining dense compacts without any liquid phase forming additives. These ceramics are suitable for high temperature applications. Some of these can also be used as cutting tool materials.

New fabrication technique namely, intermediate soft phase processing has been developed for the synthesis of ceramic-ceramic composites at moderate pressures and temperatures. The processing temperature is much below the melting point of the individual constituents of the composite. A composite of TiB_2-TiC has already been fabricated using this technique. The process can be extended to produce a number of composites with different compositions by suitable selection of intermediate soft phase and the reactant phase. The process also offers the possibility of fabricating the near-net-shape products of relatively simpler geometry.

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